Supporting Information for

Solution Stability of Organocalcium Compounds in Ethereal Media

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NMR Spectra

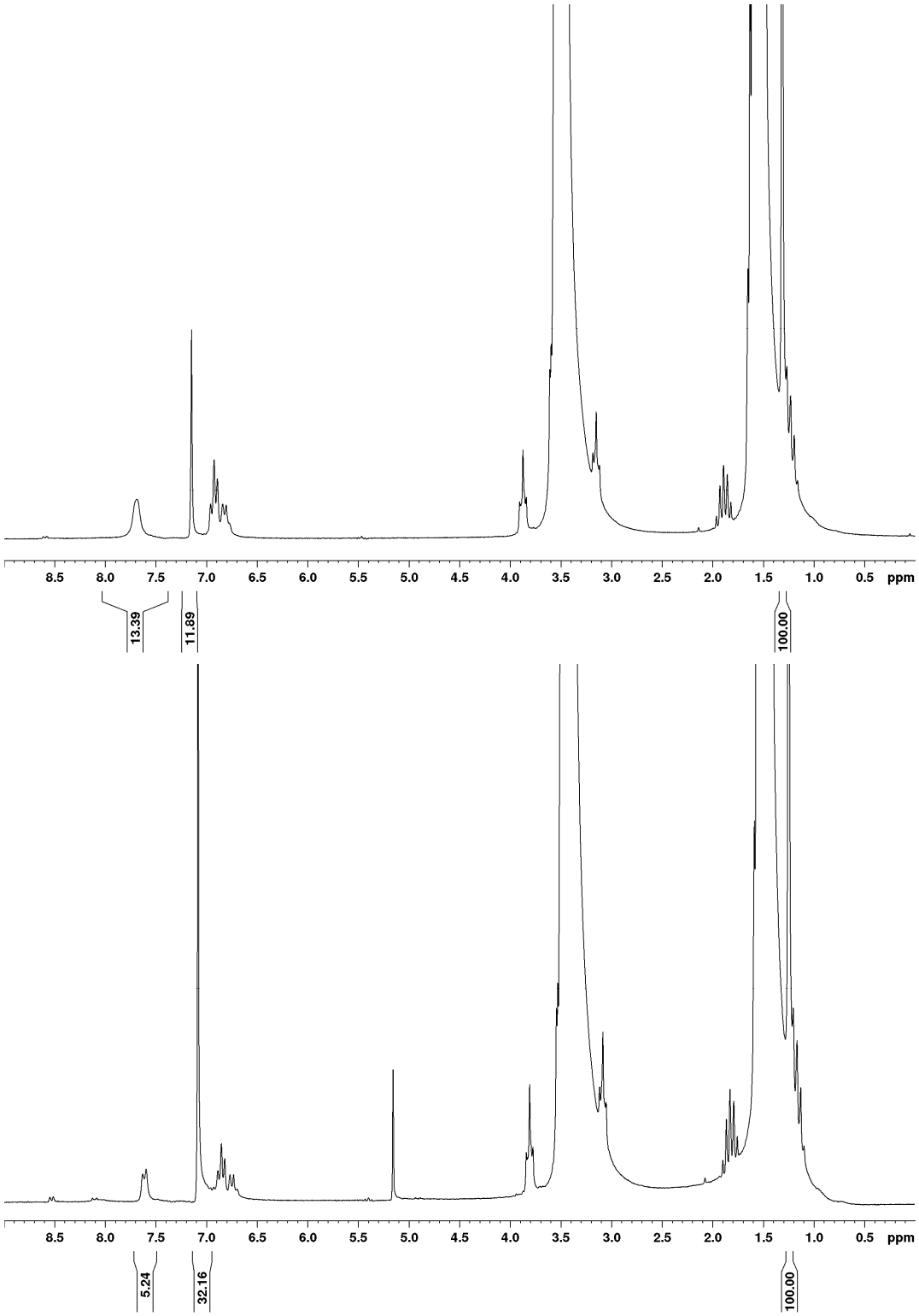

Figure S1. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.13 M solution of $[Ca(Ph)(I)(thf)_4]$ in THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 15 days.

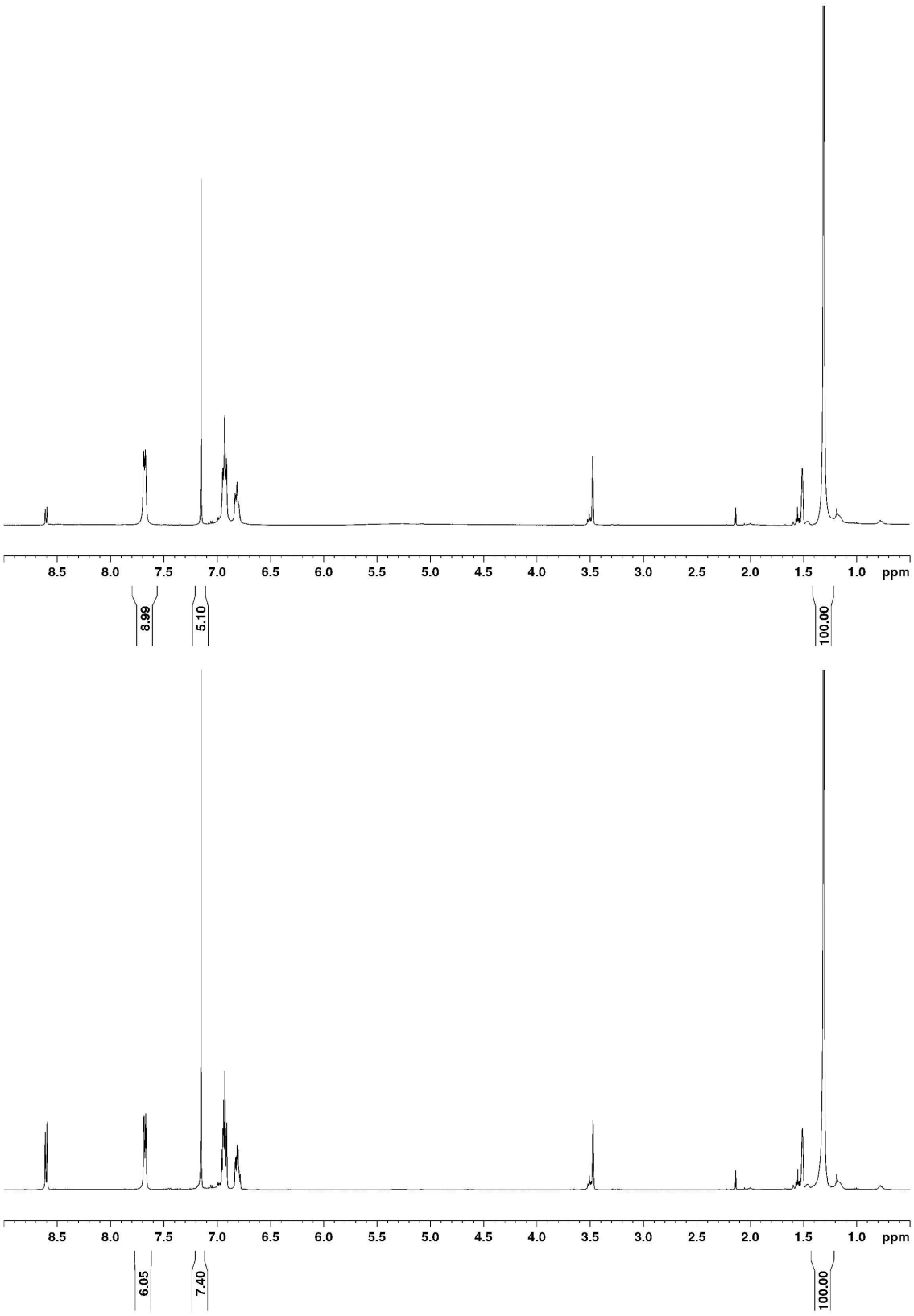

Figure S2. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.08 M solution of [Ca(Ph)(I)(thf-d_8)$_4$] in THF-d_8/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 35 days.

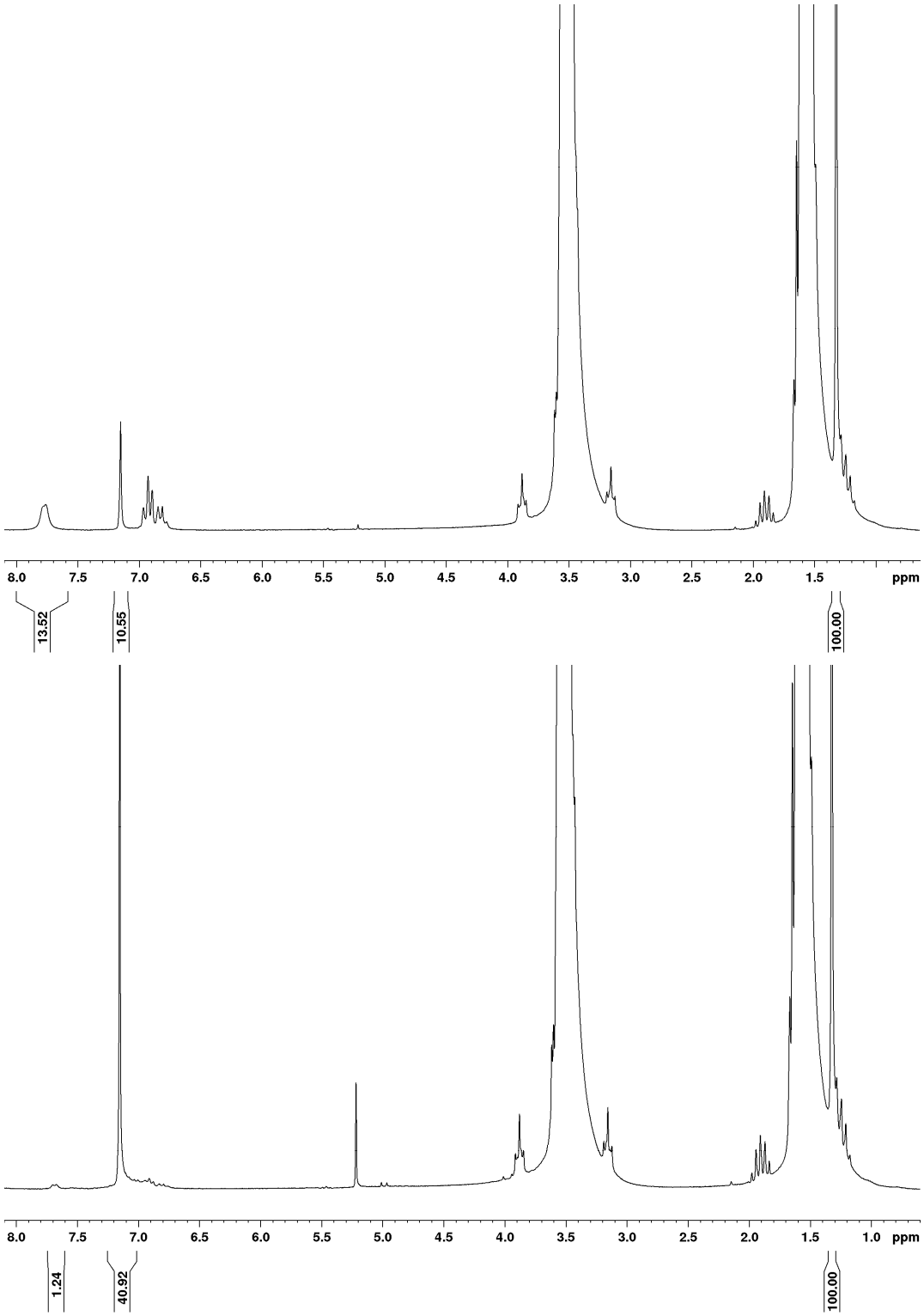

Figure S3. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.13 M solution of $[Ca(Ph)(I)(thf)_4]$ in THF/benzene-d_6 (2:1) at 50 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 1 day.

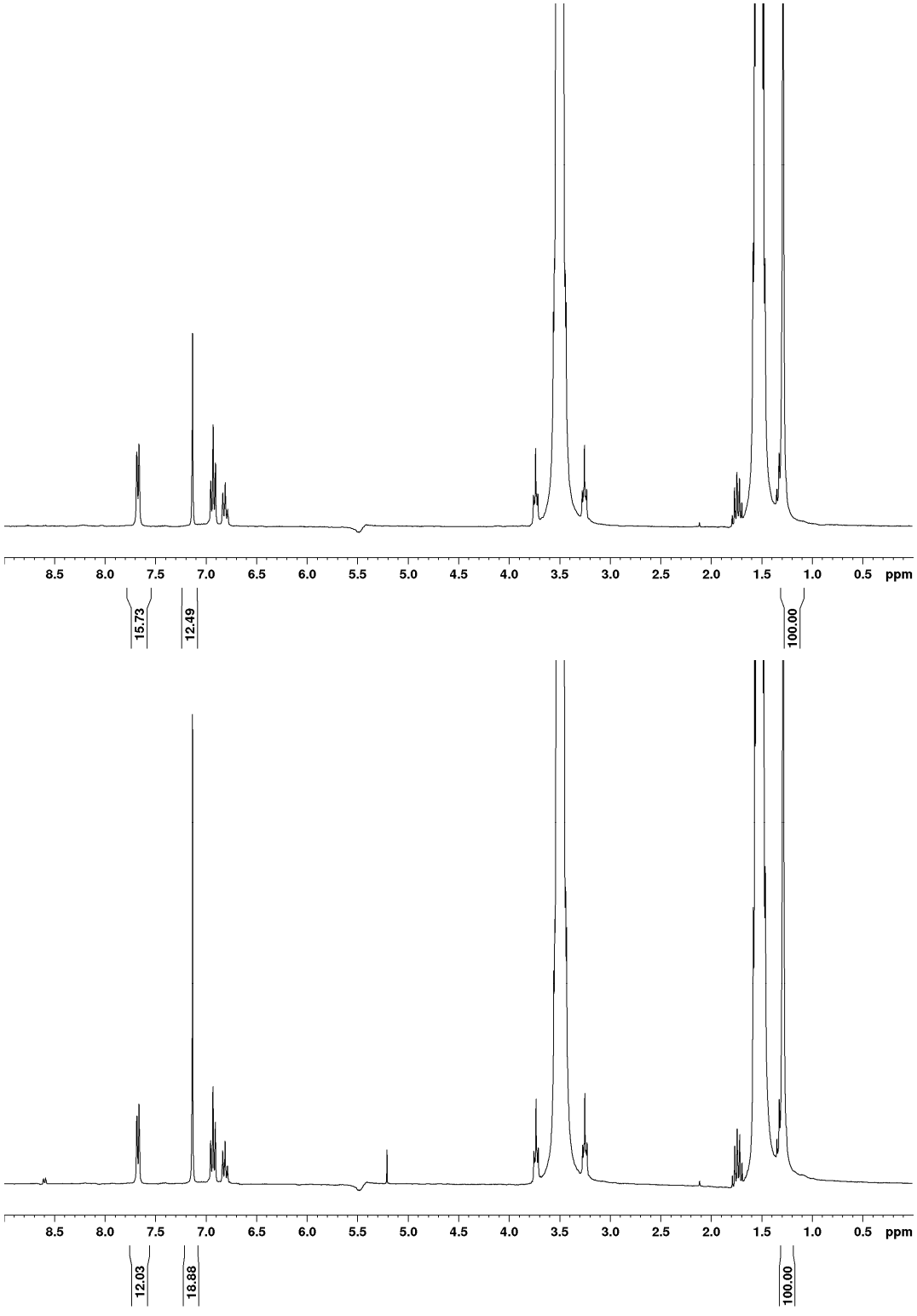

Figure S4. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.14 M solution of $[Ca(Ph)(I)(thf)_4]$ in THF/benzene-d_6 (2:1) at -7 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 118 days.

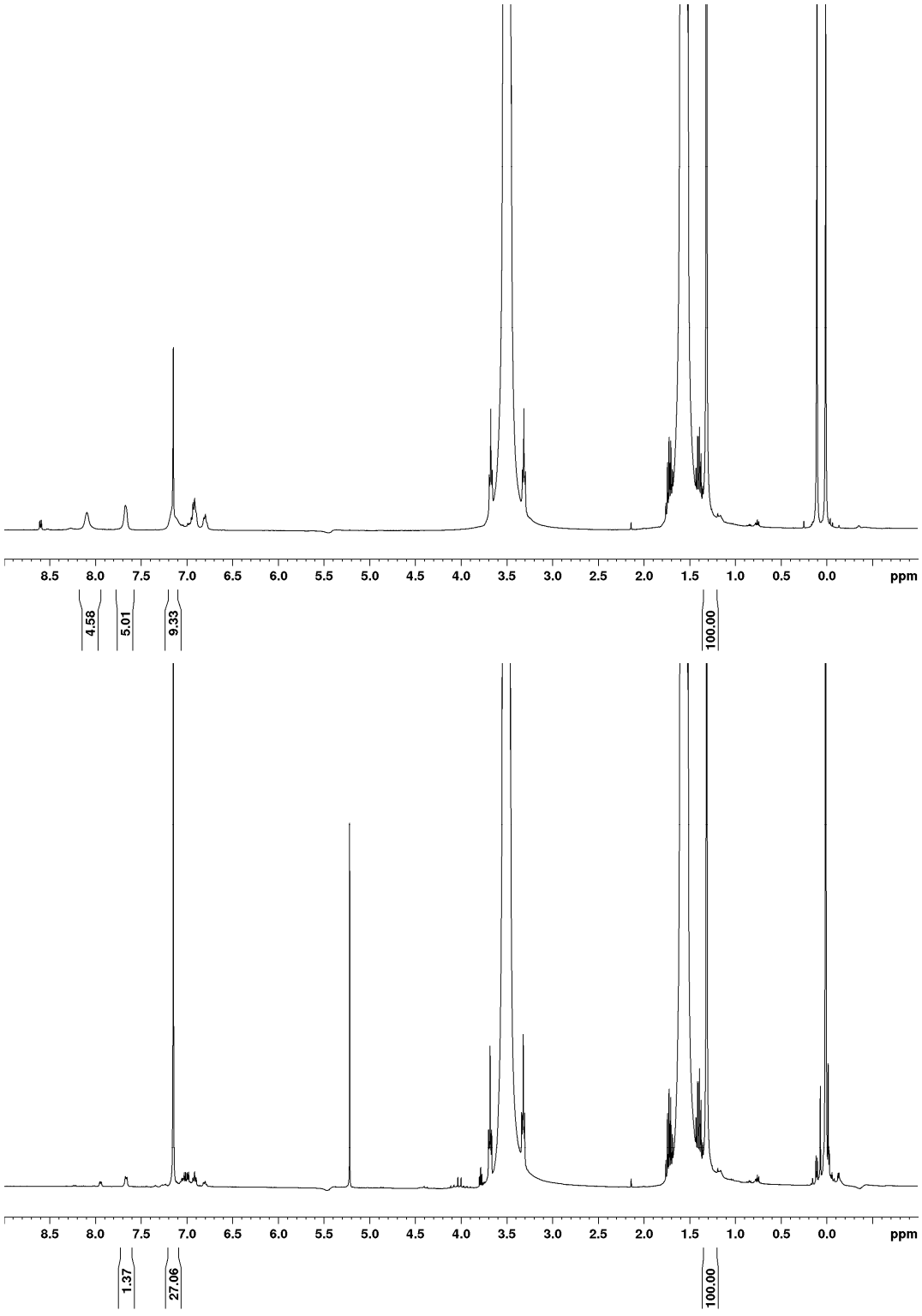

Figure S5. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.12 M solution of [Ca(Ph)(Hmds)(thf)$_3$] in THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 10 days.

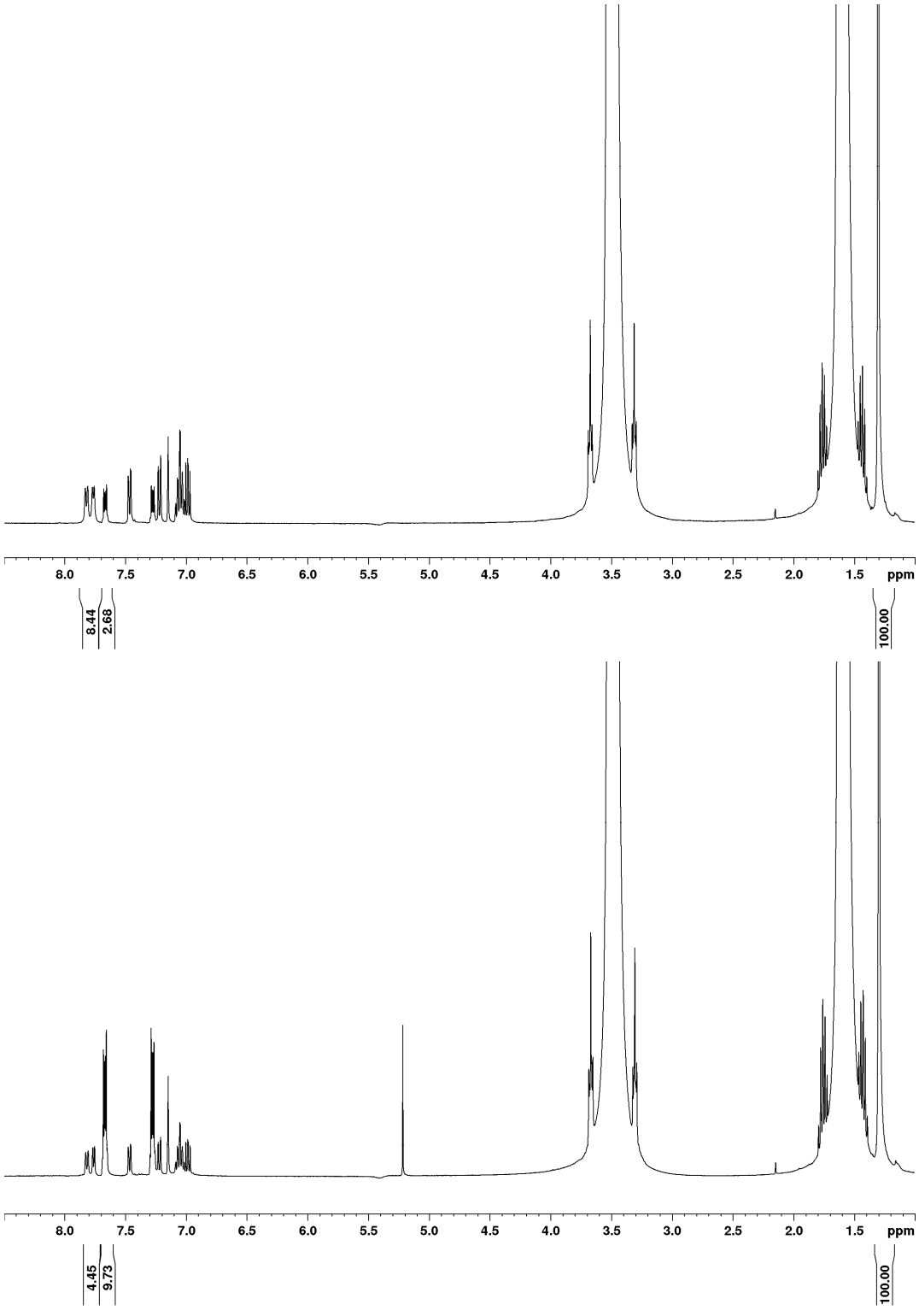

Figure S6. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.09 M solution of [Ca(Naph)(I)(thf)$_4$] in THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 42 days.

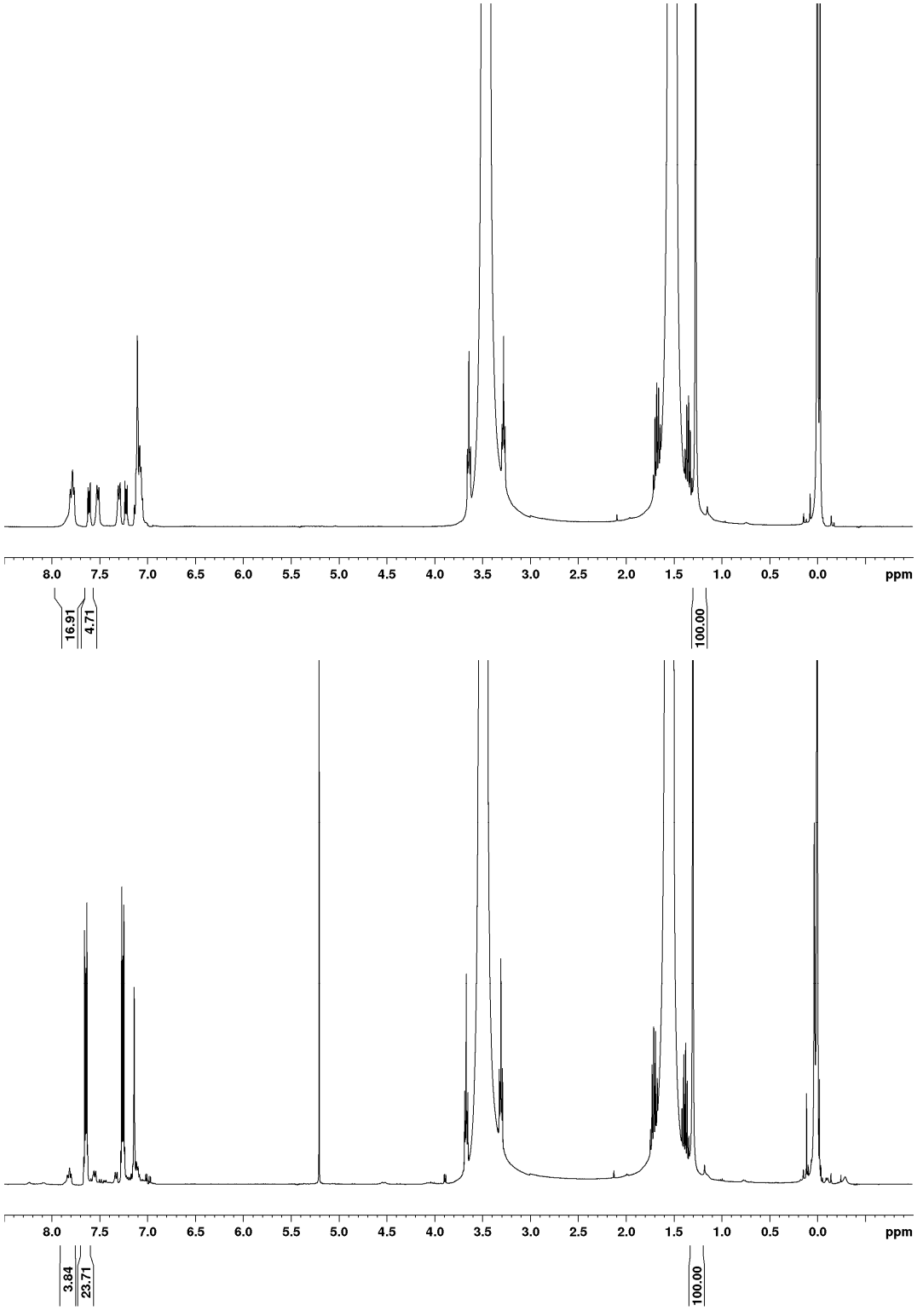

Figure S7. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.12 M solution of [Ca(Naph)(Hmds)(thf)$_3$] in THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 14 days.

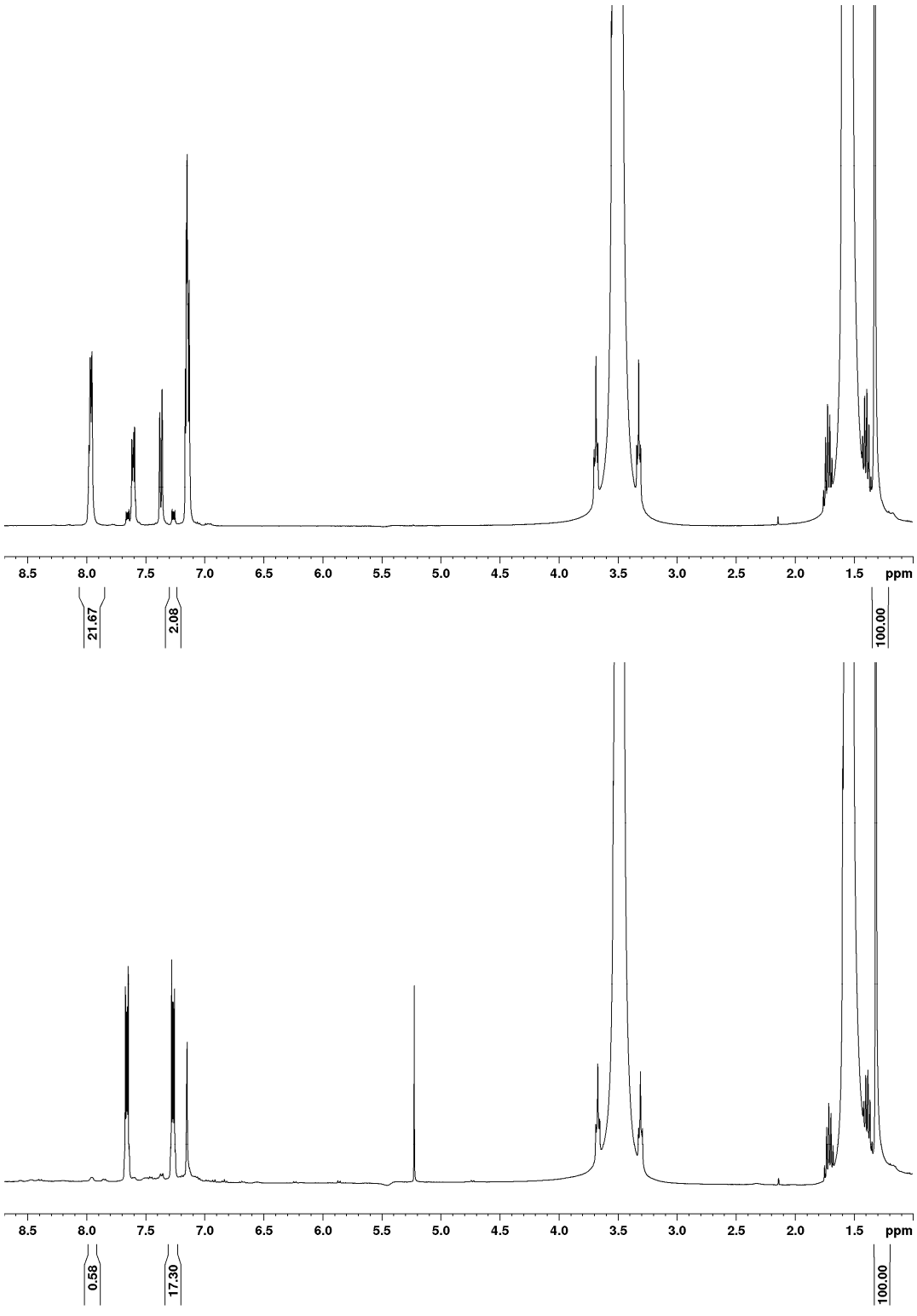

Figure S8. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.10 M solution of $[Ca(Naph)_2(thf)_4]$ in THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 13 days.

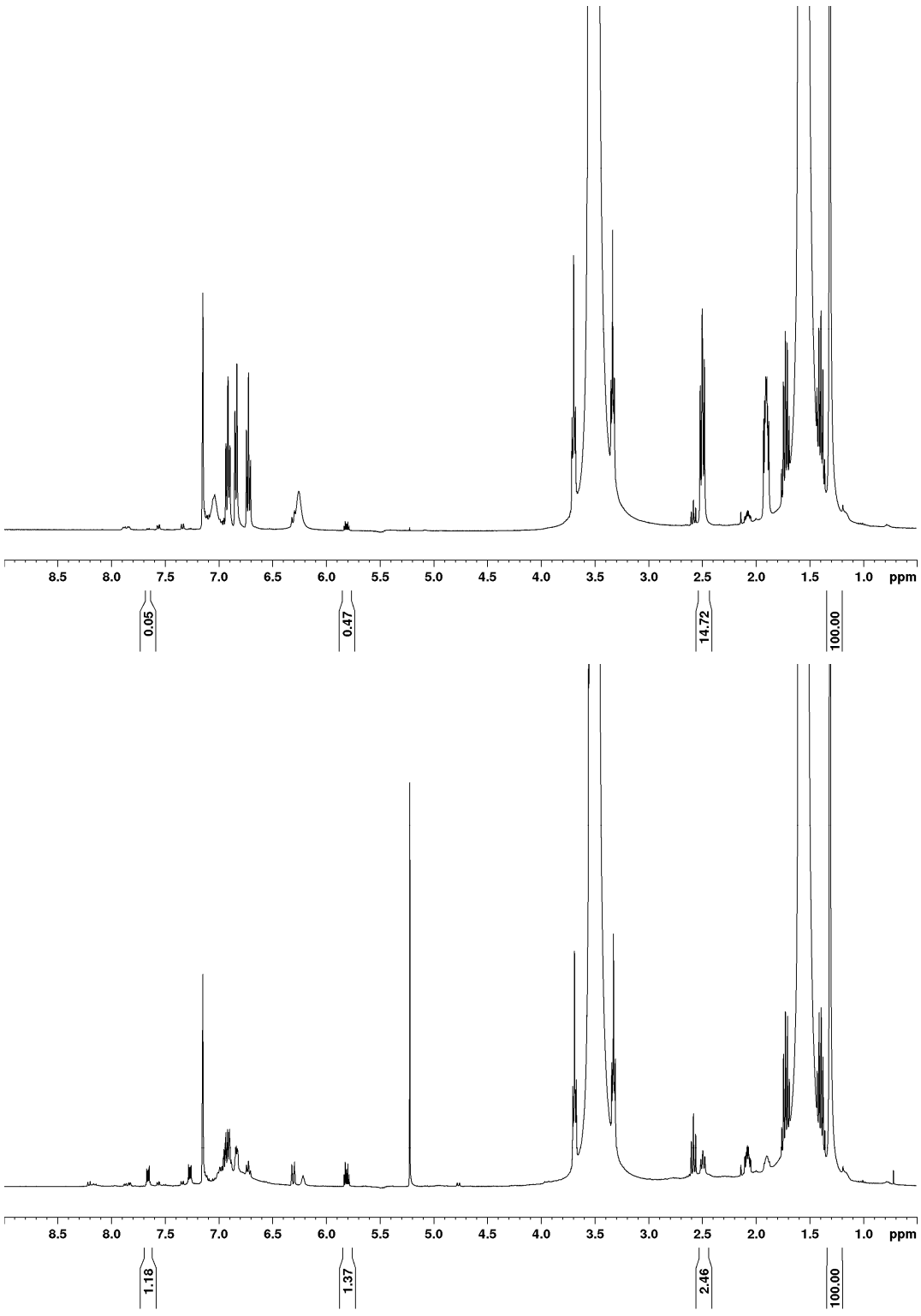

Figure S9. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.13 M solution of [Ca(1,2-Dihydronaph)(I)(thf)$_4$] in THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 15 days.

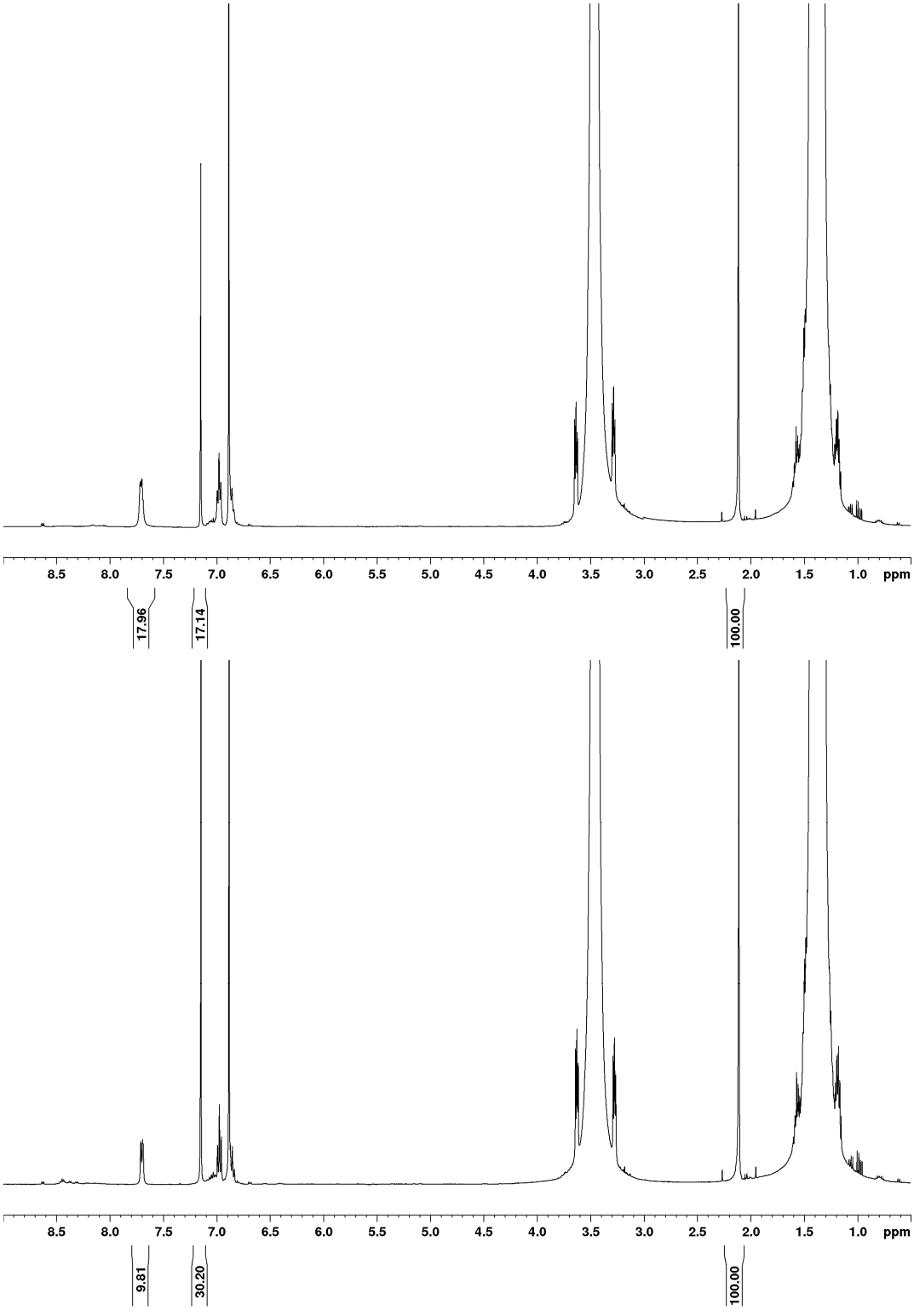

Figure S10. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.07 M solution of [Ca(Ph)(I)(thp)$_4$] in THP/benzene-d_6 (2:1) at 22 °C using *p*-xylene as internal standard. Top: beginning of the experiment. Bottom: after 19 days.

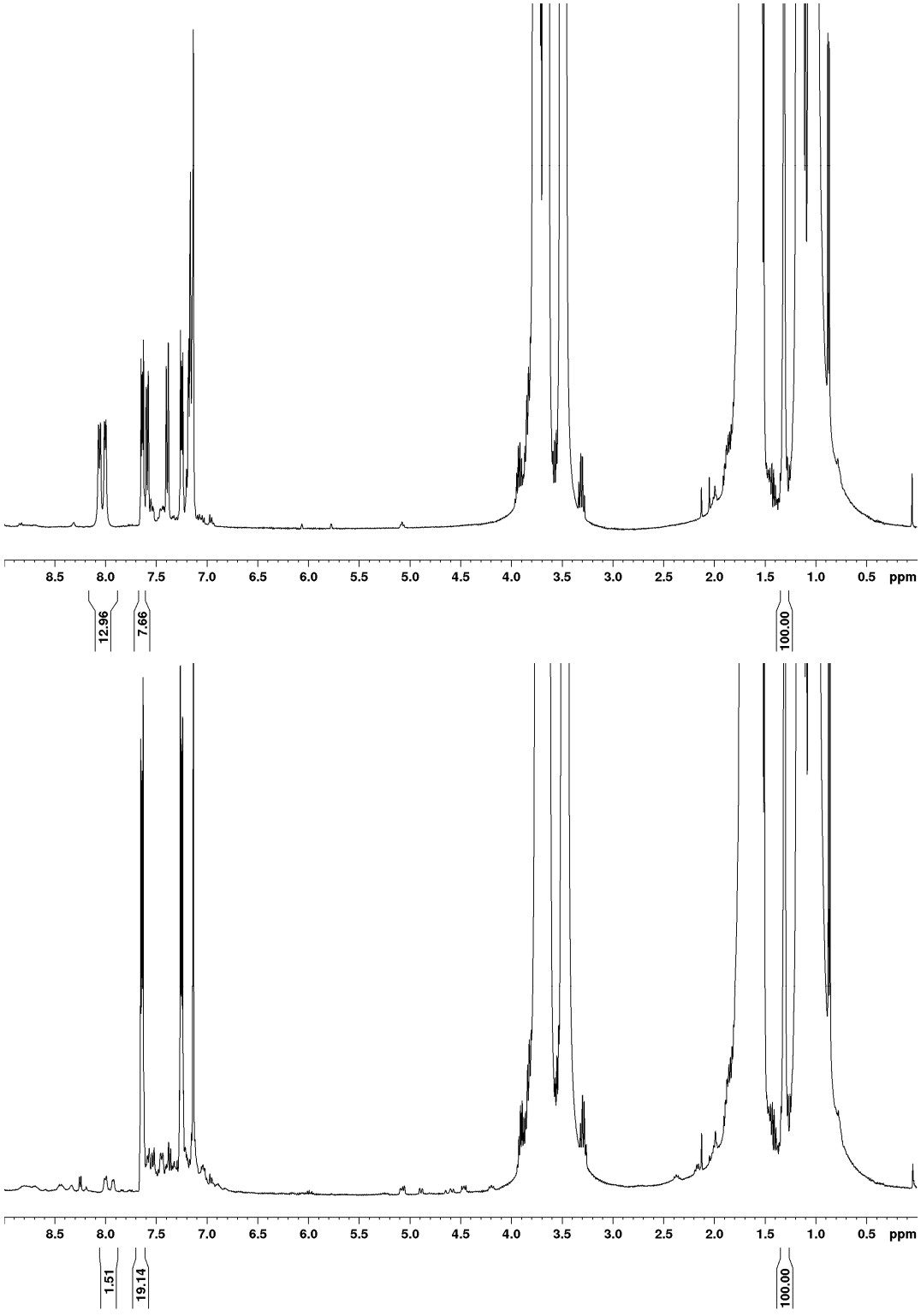

Figure S11. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.09 M solution of [Ca(Naph)(I)(Me-thf)$_4$] in Me-THF/benzene-d_6 (2:1) at 22 °C using cyclohexane as internal standard. Top: beginning of the experiment. Bottom: after 1.3 days.

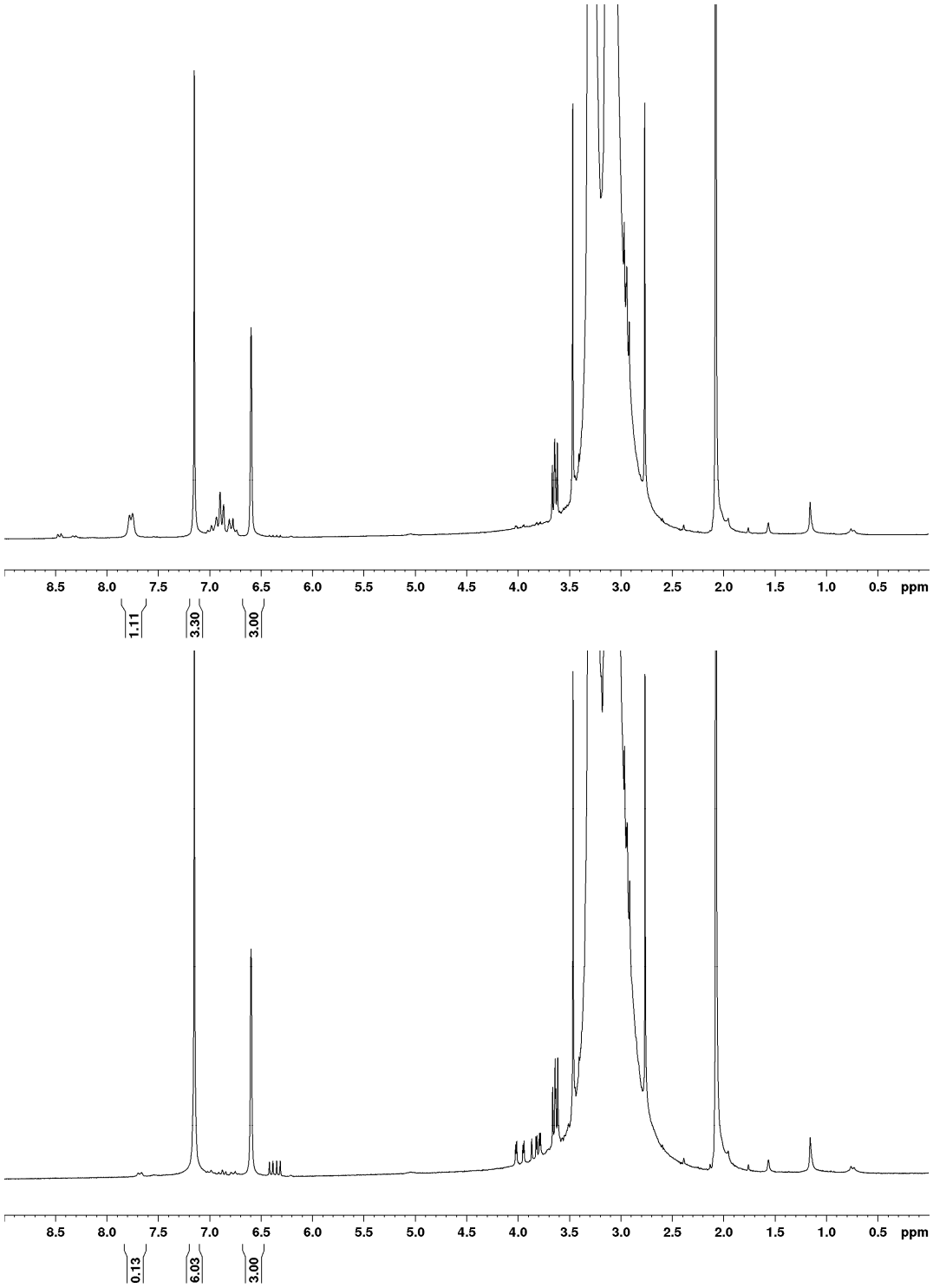

Figure S12. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.05 M solution of [Ca(Ph)(dme)$_3$]I in DME/benzene-d_6 (3:1) at 22 °C using mesitylene as internal standard. Top: beginning of the experiment. Bottom: after 1 day.

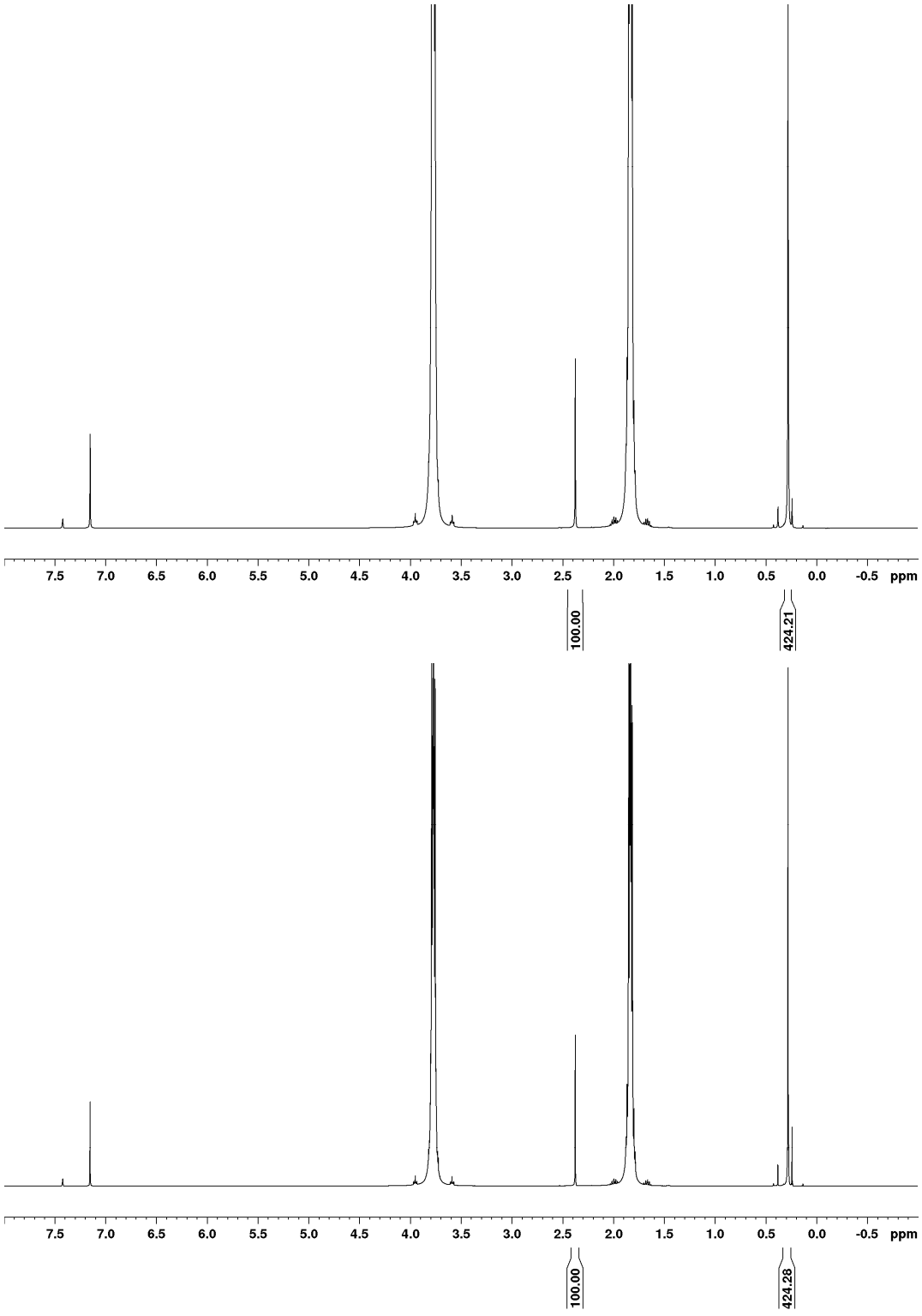

Figure S13. Time-dependent ^{1}H NMR spectra, measured at 400 MHz, of a 0.12 M solution of $[Ca(Hmds)_2(thf)_2]$ in THF/benzene-d_6 (2:1) at 22 °C using *p*-xylene as internal standard. Top: beginning of the experiment. Bottom: after 21 days.

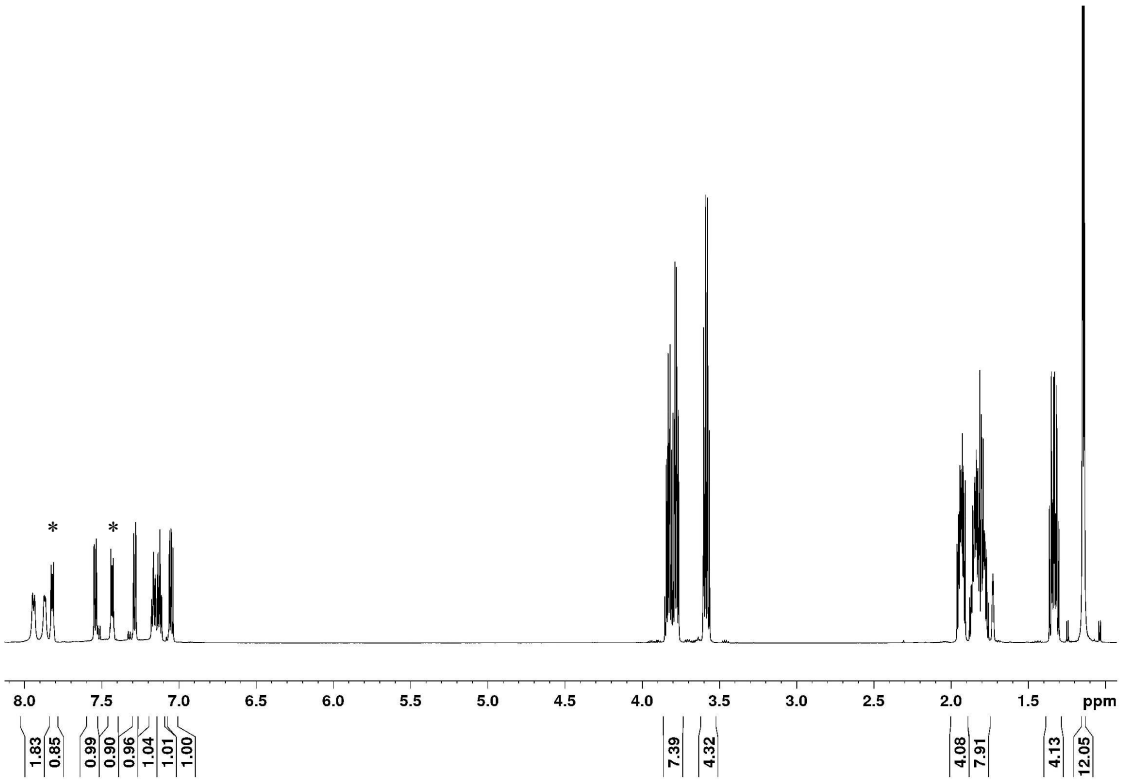

Figure S14. ^{1}H NMR spectrum of [Ca(Naph)(I)(Me-thf)$_4$] in THF-d_8 at 22 °C, measured at 600 MHz. With "*" marked signals belong to naphthalene.

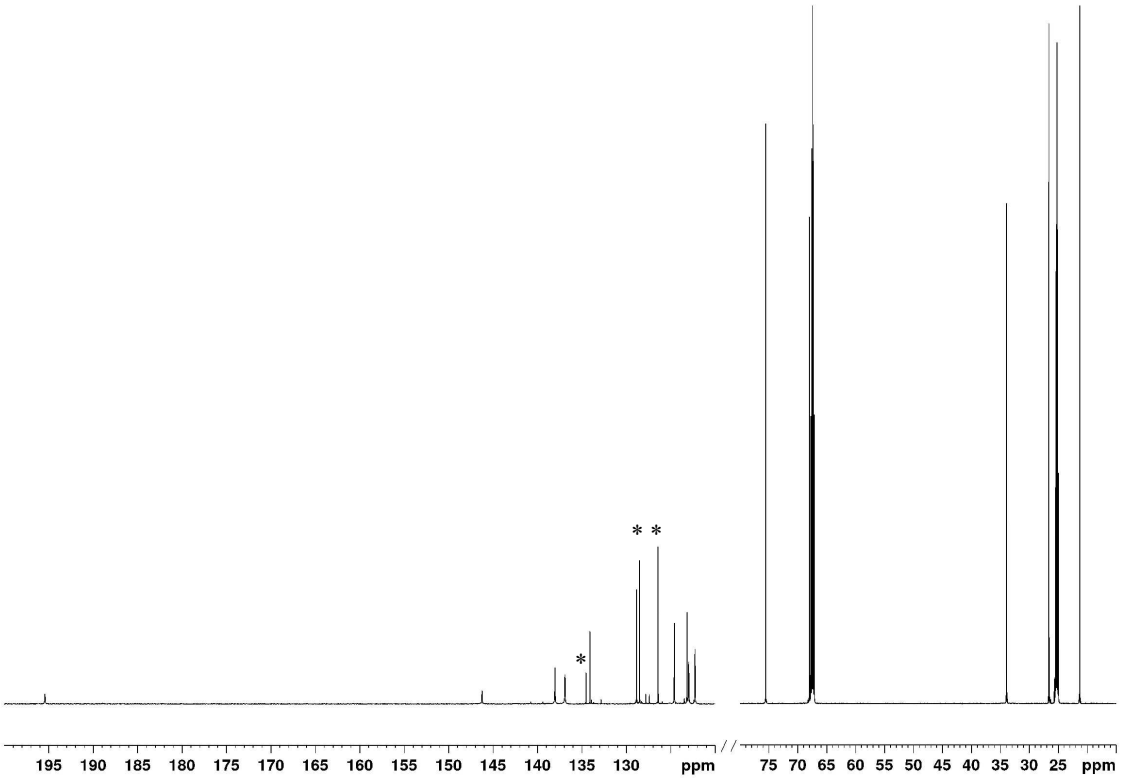

Figure S15. ^{13}C NMR spectrum of [Ca(Naph)(I)(Me-thf)$_4$] in THF-d_8 at 22 °C, measured at 150.9 MHz. With "*" marked signals belong to naphthalene.

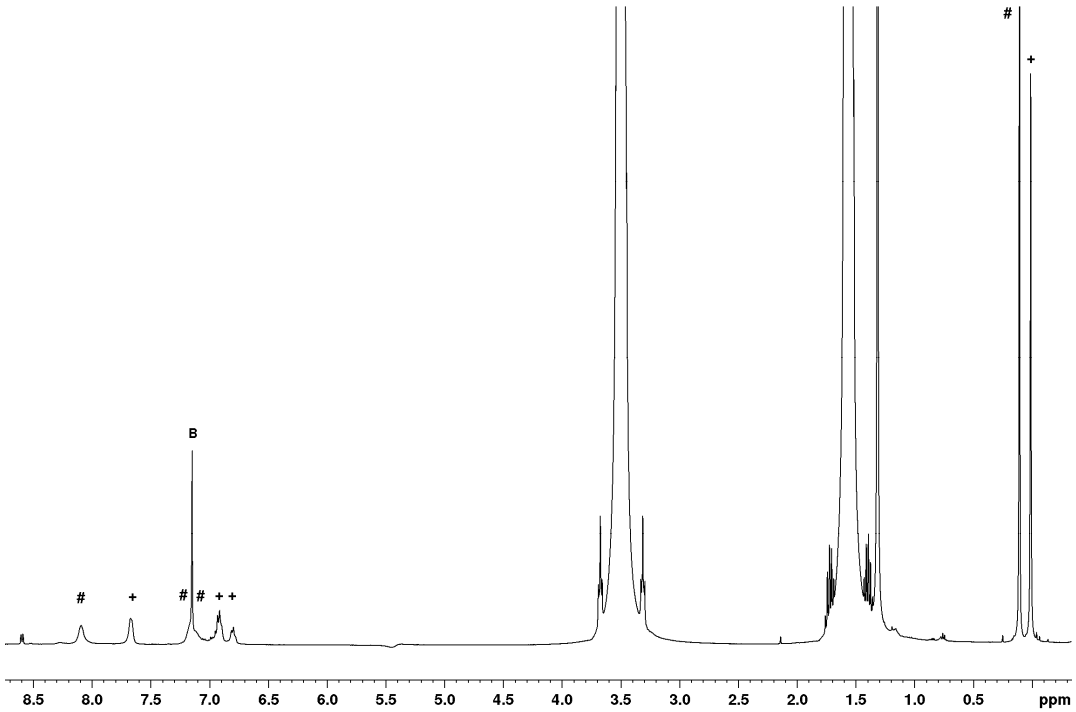

Figure S16. ^{1}H NMR spectrum of a 0.12 M solution of [Ca(Ph)(Hmds)(thf)$_3$] in THF/benzene-d_6 (2:1) at 22 °C, measured at 400 MHz. With "#" marked signals belong to the primary species of [Ca(Ph)(Hmds)(thf)$_3$], with "+" marked signals belong to the secondary species of [Ca(Ph)(Hmds)(thf)$_3$] and the signal marked with "B" belongs to benzene.

NMR data for both species:

^{1}H NMR (THF/ benzene-d_6, 400 MHz): δ 1.56 (m, CH_2 THF), 3.49 (m, OCH_2 THF), 7.15 (s, CH benzene).
primary species: δ 0.11 (s, $SiCH_3$), 7.06-7.25 (m, *m*- and *p*-CH phenyl, overlapping signals), 8.09 (bs, o-CH phenyl).
secondary species: δ 0.01 (s, $SiCH_3$), 6.80 (m, *p*-CH phenyl), 6.92 (m, *m*-CH phenyl), 7.68 (m, o-CH phenyl).

The signals of the secondary species deviate only slightly from the literature values of [Ca(Ph)(Hmds)(thf)$_3$] due to the change of the solvent system. [S1]

Plots with units of concentration

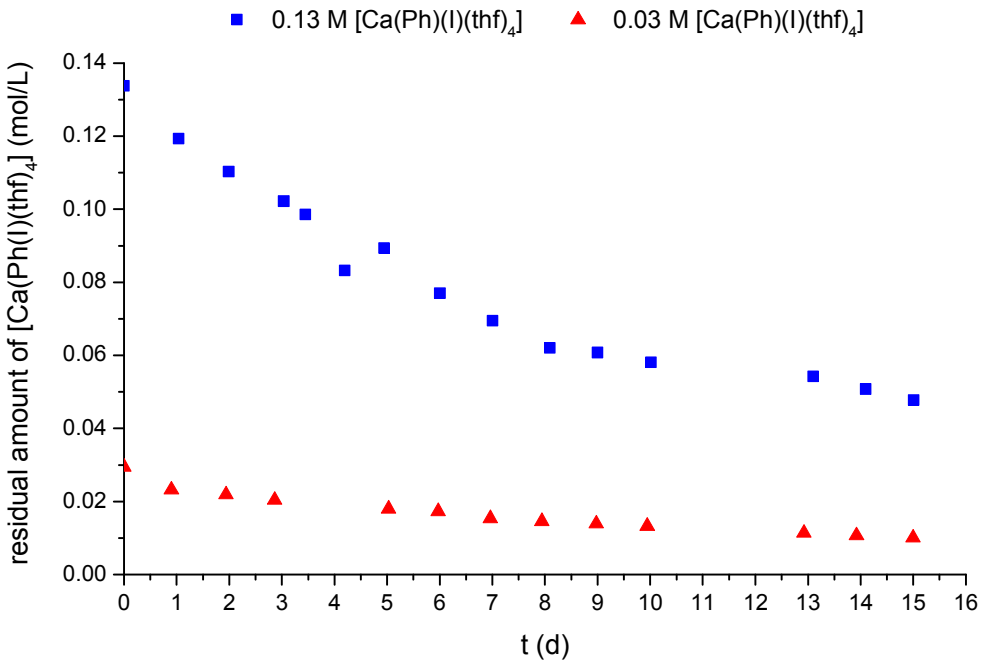

Figure S17. Decay of the primary organocalcium species of [Ca(Ph)(I)(thf)$_4$] solutions in THF/benzene-d_6 (2:1) with different concentrations at 22 °C.

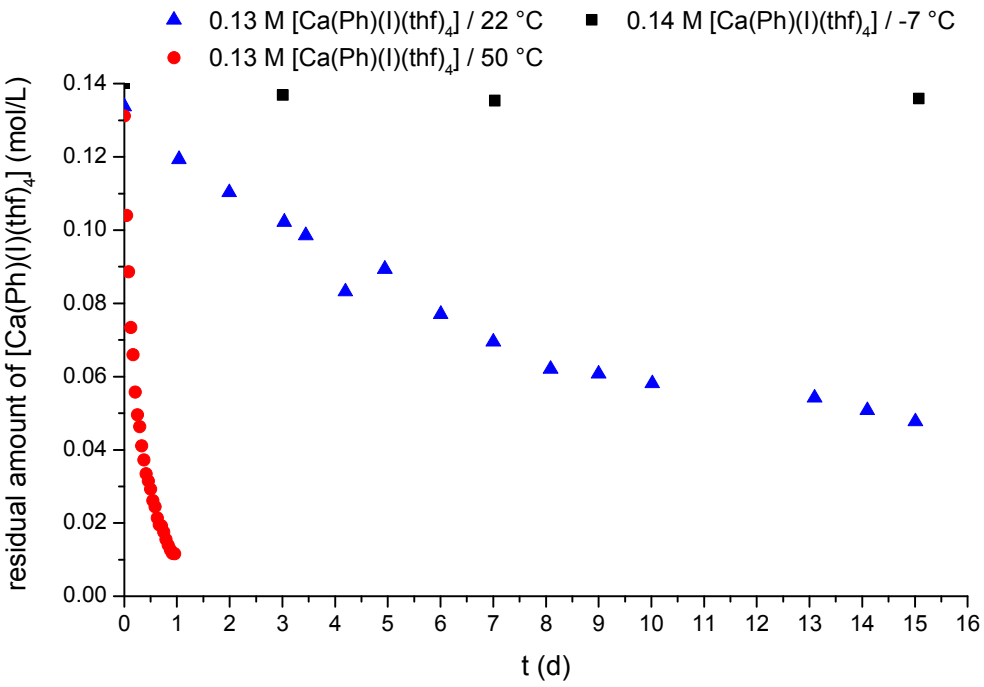

Figure S18. Decay of the primary organocalcium species of [Ca(Ph)(I)(thf)$_4$] solutions in THF/benzene-d_6 (2:1) at different temperatures.

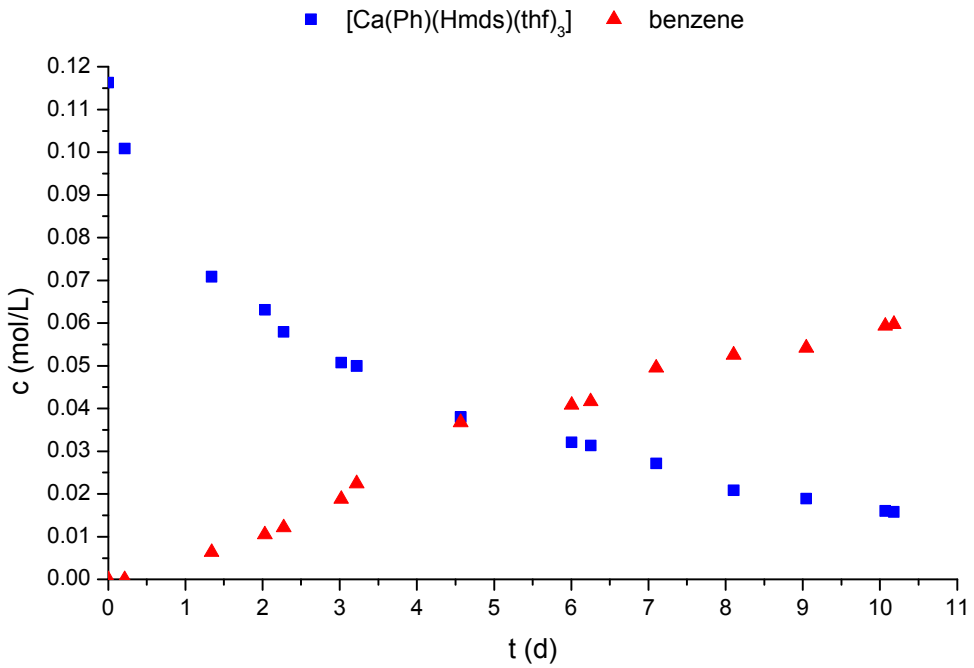

Figure S19. Time-dependent trend of the concentration of benzene and the primary organocalcium species of a 0.12 M solution of [Ca(Ph)(Hmds)(thf)$_3$] in THF/benzene-d_6 (2:1) at 22 °C.

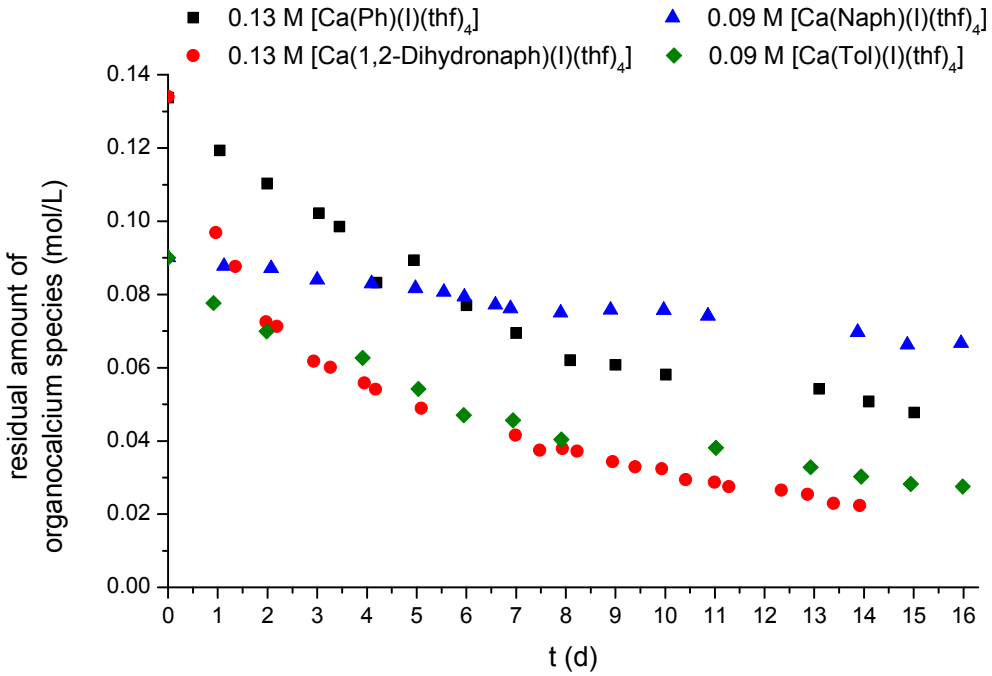

Figure S20. Decay of organocalcium derivatives of the type [Ca(R)(I)(thf)$_4$] (R = Ph, Tol, Naph, 1,2-Dihydronaph) in THF/benzene-d_6 solutions at 22 °C.

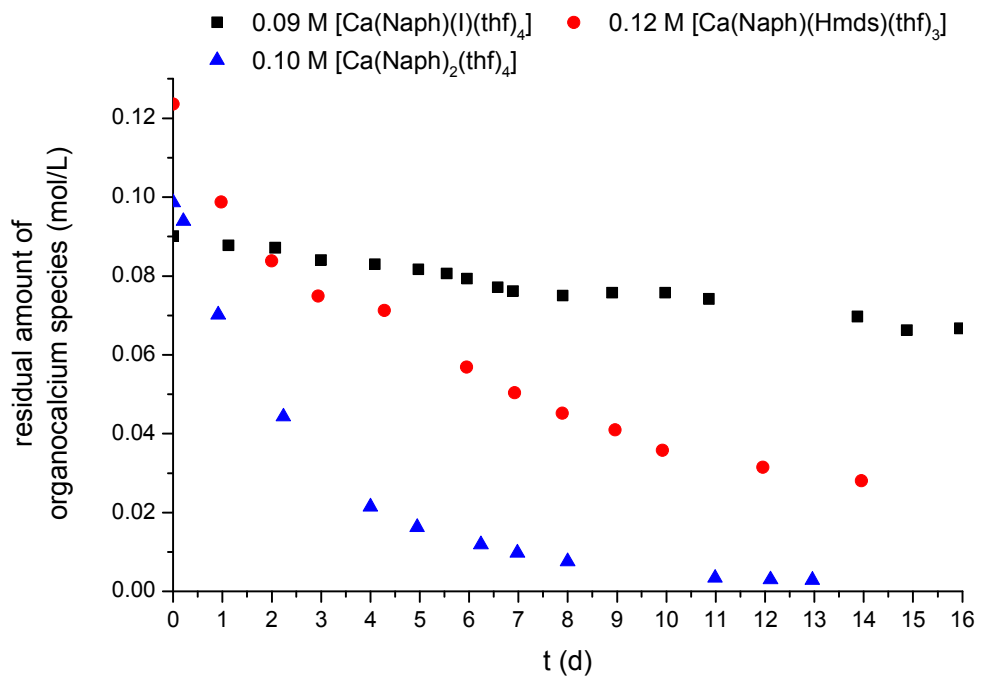

Figure S21. Time dependent decay of organocalcium derivatives of the type [Ca(Naph)(X)(thf)$_4$] (X = I, Hmds, Naph) in THF/benzene-d_6 (2:1) solutions at 22 °C.

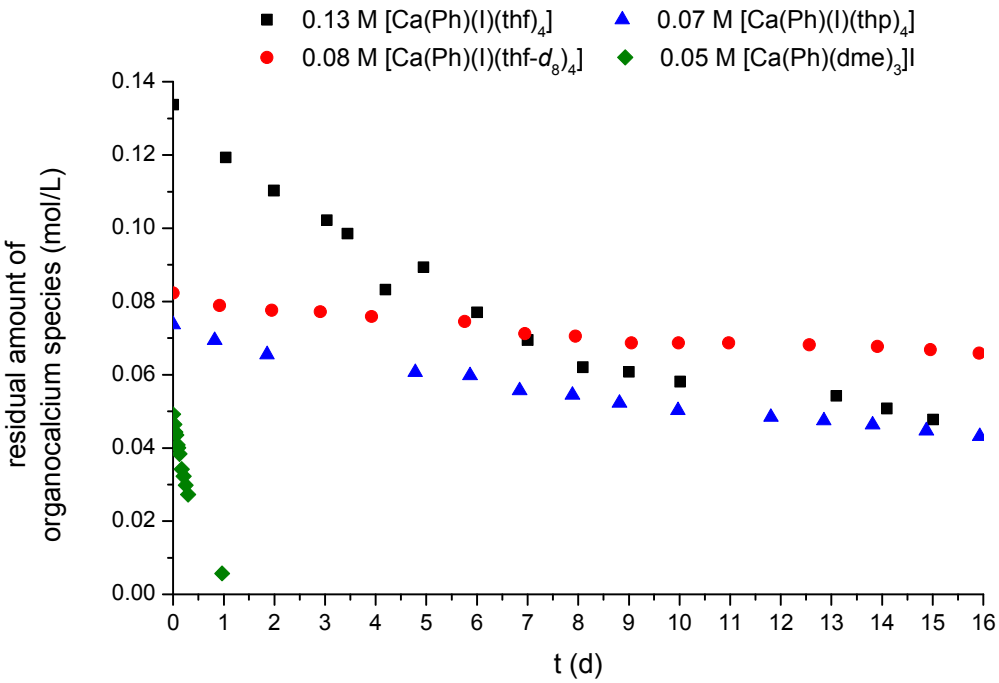

Figure S22. Decay of the primary organocalcium species of complexes of the type [Ca(Ph)(I)(L)$_4$] (L = thf, thf-d_8, thp) in a solution of L/benzene-d_6 (2:1), as well as the decay of [Ca(Ph)(dme)$_3$]I in a solution of DME/benzene-d_6 (2:1) s at 22 °C.

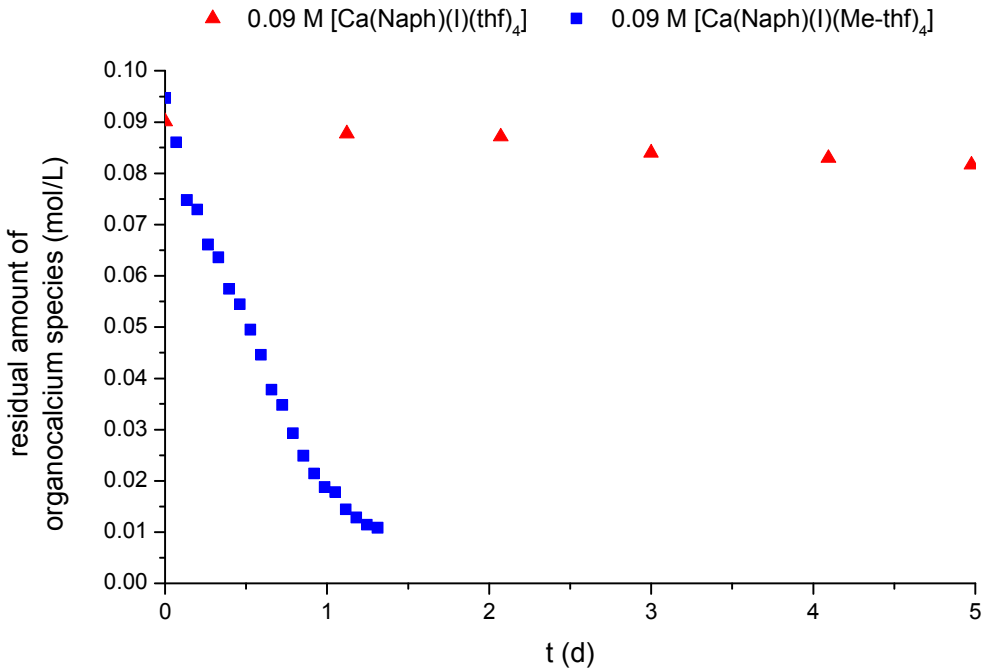

Figure S23. Decay of the primary organocalcium species of complexes of the type [Ca(Naph)(I)(L)$_4$] (L = thf, Me-thf-d_8) in a solution of L/benzene-d_6 (2:1) at 22 °C.

Crystal structure

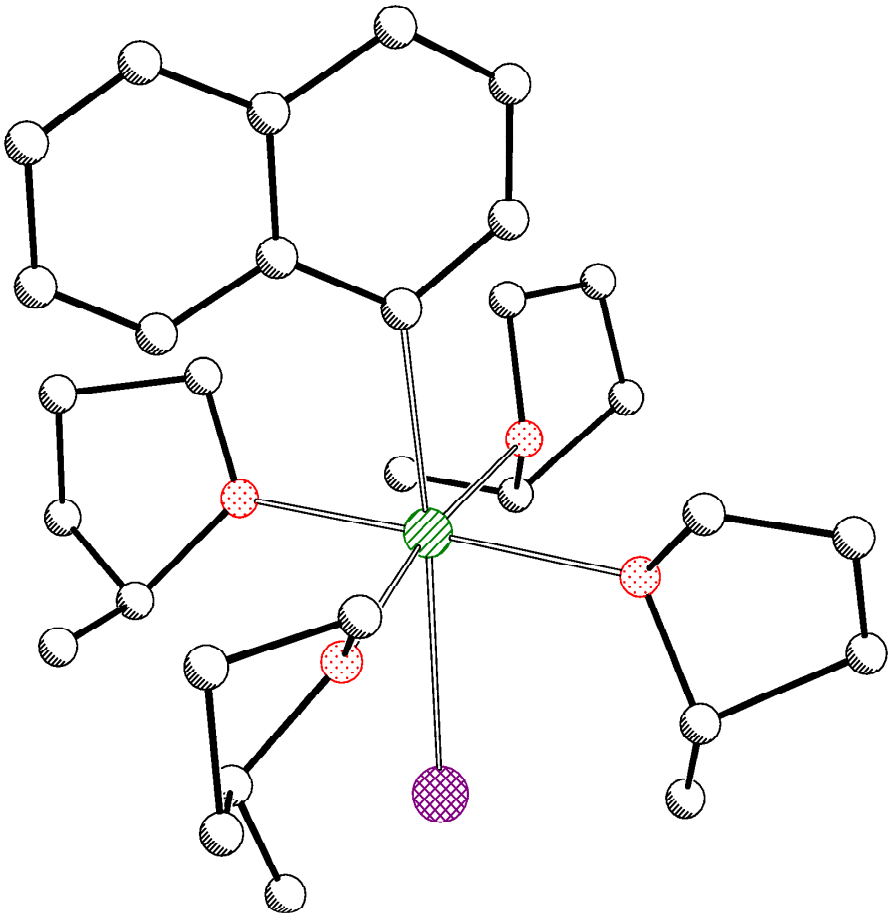

Figure S24. Structural motif of [Ca(Naph)(I)(Me-thf)$_4$]. (color code: green calcium, red oxygen, purple iodine, white carbon)

The data obtained by single crystal X-ray diffraction experiment suffers from a heavy disorder of the methyl group of α-methyltetrahydrofuran as a result of its racemic nature. For each of the four molecules present in [Ca(Naph)(I)(Me-thf)$_4$], the methyl group can in principle adopt four different positions. While the positions of all other atoms could be satisfactorily refined, it was not possible to treat the disorder of the methyl groups properly. The methyl groups were added as constraints in one of the four positions possible.

Crystal Data for structural motif of [Ca(Naph)(I)(Me-thf)$_4$]: colourless prism, size 0.059 × 0.048 × 0.052 mm^3, orthorhombic, space group Pnma, a = 17.6889(4), b = 13.7527(2), c = 12.6503(3) Å, V = 3077.44(11) Å^3 , T= -140(2) °C, Z = 4, $\rho_{calcd.}$ = 1.257 g·cm^{-3}, μ (Mo-K$_\alpha$) = 12.31 cm^{-1}, F(000) = 1200, 16095 reflections in h(-22/17), k(-16/17), l(-16/14), measured in the range 2.19° ≤ Θ ≤ 27.46°, completeness Θ_{max} = 99.5%, 3655 independent reflections, 3177 reflections with $F_o > 4\sigma(F_o)$, largest difference peak and hole: 1.585 / -1.107 e Å^{-3}.

Literature

S1 Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2007**, *26*, 1077-1083.